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(54) **Layered, hexagonal lithium manganese oxide as a positive electrode active material for lithium battery, method for producing the same, and lithium battery containing the same**

Hexagonales, schichtförmiges Lithiummanganat als aktives Material für die positive Elektrode einer Lithiumbatterie, Verfahren zu dessen Herstellung, und dieses enthaltende Lithiumbatterie

Manganate de lithium d'une structure hexagonale, stratifié, comme matériau actif pour une électrode dans une batterie au lithium, procédé de production de celui-ci, et batterie au lithium le contenant

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a positive electrode active material for a lithium battery, a method for producing the same, and a battery containing the same in the positive electrode thereof.

2. Description of the Related Art

[0002] With the recent development of portable electronic equipment, batteries of higher performance have been demanded. Lithium ion batteries using a carbon material in the negative electrode and lithium cobaltate (LiCoO_2), which is a composite oxide having a layer structure, in the positive electrode have been put to practical in a nonaqueous battery having a high working voltage and a high energy density. Lithium nickelate (LiNiO_2), which is also a compound having the same layered crystal structure as the lithium cobaltate in which lithium ions are intercalated between layers of NiO_6 octahedral sharing edges.

[0003] Lithium nickelate is generally prepared by mixing a nickel source selected from $\text{Ni}(\text{NO}_3)_2$, $\text{Ni}(\text{OH})_2$, NiCO_3 , NiO , NiOOH , etc. and a lithium source selected from LiOH , LiNO_3 , Li_2CO_3 , Li_2O_2 , etc., and subjecting the mixture to a heat treatment at about 600 to 900°C in an oxygen stream.

[0004] Since cobalt or nickel used in these active materials is expensive for scarcity, less expensive active materials for a positive electrode has been sought. For example, Li -containing manganese composite oxide (LiMn_2O_4) having a spinel structure has been proposed, but its theoretical capacity of 148 mAh/g is low, and the reduction in capacity increases with charge and discharge cycles.

[0005] LiMnO_2 has been proposed as a promising active material for batteries with higher performance. Among various phases exhibited by LiMnO_2 , two phases, whose crystal structure have been well characterized, are a high temperature orthorhombic phase (Pm-nm) and a low temperature tetragonal phase ($\text{I4}_1/\text{amd}$). Both structures involve cubic close packing but they differ in the arrangement of the ordering of the lithium and manganese cations. The tetragonal form $\text{Li}_2\text{Mn}_2\text{O}_4$ is prepared by electrochemically or chemically intercalating lithium into the spinel LiMn_2O_4 [Mat. Res. Bull. 18 (1983)461 & 18(1983)1375; J. Electrochem. Soc. 138 (1991)2864 & 139(1992)937]. The orthorhombic phase has been prepared mainly by the solid state reaction at high temperature using different precursors [J. Phys. Chem. Solid. 3(1957)20 & 318; J. Phys. Radium 20 (1959)155; J. Anorg. Allg. Chem. 417(1975)1; Mater. Res. Bull. 28(1993)1249]. However, orthorhombic LiMnO_2 was reported to be prepared at low temperature

using the solid state reaction by heating a mixture of $\gamma\text{-MnOOH}$ and LiOH at 300 to 450°C [Chem. Express, 7(1992)193]. An other process for preparing the orthorhombic LiMnO_2 at a temperature less than 100°C by ion exchange was reported. [J. Electrochem. Soc. 140(1993)3396; Unexamined Japanese Patent Publication (kokai) No. 6-349494] In this case, the exchange was carried out by refluxing $\gamma\text{-MnOOH}$ under boiling condition in LiOH solution. So far, LiMnO_2 isostructural with layered LiNiO_2 or LiCoO_2 has not yet been synthesized.

[0006] Referring to LiMnO_2 having a layer structure, J. Solid State Chem., 104(1993)464 and U.S. Patent 5,153,081 report that LiMnO_2 having a monoclinic layer structure can be obtained by acid leaching of Li_2O out of Li_2MnO_3 . In the first step, Li_2MnO_3 was prepared by reacting electrolytic manganese dioxide (EMD) with a stoichiometric quantity of Li_2O_3 . The obtained material was then delithiated using H_2SO_4 at room temperature for 64 hours.

[0007] The thus obtained substance exhibits a discharge voltage of 3 V vs. Li/Li^+ . Although the reaction product exhibits a new X-ray diffraction peak at $2\theta=19.5^\circ$, most of the other peaks correspond to the starting material which is Li_2MnO_3 (U.S. Patent 5,153,081). Ignoring the fact that most of the peaks are assigned to the starting Li_2MnO_3 , the inventors of U.S. Patent 5,153,081 identify the product to be a substance having a layer structure based on the peak at $2\theta=19.5^\circ$, but the identification seems to be decisively unreasonable. In this case, the product should rather be regarded as a lithium manganese oxide having a spinel structure as a basic skeleton, such as $\text{Li}_2\text{Mn}_4\text{O}_9$ or $\text{Li}_4\text{Mn}_5\text{O}_{12}$.

[0008] Further, J. Solid State Chem., 104(1993)464 reports a substance having a layer structure whose X-ray diffraction pattern is different from those of LiNiO_2 or LiCoO_2 . While not entering into details about structural refinement of the substance, the report based their layered structure on the assumption that removal of Li_2O from Li_2MnO_3 causes a shearing of the closed-packed oxygen planes to yield an oxygen array in the obtained material comprised of alternate layers of trigonal prisms where lithium is located and sheets of edge-shared octahedra where manganese is located. In this case, the manganese ions remain in alternate layers and do not migrate to the lithium layers during the leaching process, and the lithium layer is arranged in a zig-zag fashion with lithium ions in a trigonal prismatic coordination.

[0009] Unexamined Japanese Patent Publication (kokai) No. 7-223819 reports that LiMnO_2 having a layer structure with a lattice constant of $a=3.321 \text{ \AA}$ and $c=4.730 \text{ \AA}$ is obtained by electrolysis method. This material is not isostructural with LiNiO_2 . Thus, no LiMnO_2 having a layer structure similar to that of LiNiO_2 or LiCoO_2 , has been synthesized yet.

[0010] As stated above, although 4.0 V type LiMn_2O_4 having a spinel structure has been proposed as an in-

expensive Li-containing manganese composite oxide, the theoretical capacity is inferior to oxide compounds having a hexagonal layer structure, such as LiNiO_2 (theoretical capacity: 275 mAh/g) and LiCoO_2 (theoretical capacity: 274 mAh/g). In addition, the charge and discharge cycle characteristics are better in layered oxide materials. Therefore, development of an inexpensive active material having a layer structure similar to that of LiNiO_2 or LiCoO_2 and establishment of synthesis therefore have been keenly demanded, but a useful method of synthesis has not yet been established.

SUMMARY OF THE INVENTION

[0011] It is an object of the present invention to prepare lithium manganate with a structure different from the spinel structure of known LiMn_2O_4 but is analogous to the hexagonal layer structure of lithium cobaltate or lithium nickelate, having a space group of $R\bar{3}m$, and is therefore expected to exhibit increased activity as a positive electrode active material for lithium batteries.

[0012] The present invention provides a positive electrode active material for lithium batteries which comprises lithium manganate having a hexagonal layer structure with space group of $R\bar{3}m$ and exhibits continuous discharge voltage characteristics between 4.5 V and 2 V vs. Li/Li^+ . The active material according to the present invention has a theoretical capacity of 286 mAh/g.

[0013] The present invention also provides a method for producing such a positive electrode active material, and a battery containing the positive electrode active material.

[0014] The positive electrode active material according to the present invention undergoes homogeneous reaction to exhibit continuous discharge voltage characteristics between 4.5 V and 2.0 V vs. Li/Li^+ . The discharge characteristics are stable upon cycling, providing a long battery life. The active material of the invention is inexpensive and economical.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Fig. 1A shows an X-ray diffraction pattern of LiMnO_2 having a layer structure according to the present invention;

Fig. 1B shows an X-ray diffraction pattern of LiNiO_2 having a layer structure;

Fig. 1C shows an X-ray diffraction patterns of LiMnO_2 with orthorhombic structure obtained by a conventional solid phase reaction;

Fig. 2 shows an illustration of the layer structure of LiMnO_2 according to the present invention; and

Fig. 3 shows typical discharge characteristics of LiMnO_2 according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The lithium manganate according to the invention is not the known LiMnO_2 obtained by the reaction between $\gamma\text{-MnOOH}$ and LiOH in a solid phase calcination process but LiMnO_2 which is obtained by a hydrothermal reaction of $\gamma\text{-MnO}_2$ in an LiOH solution and has a layer structure similar to the structure of LiNiO_2 or LiCoO_2 . The lithium manganate of the present invention can be applied as a positive electrode active material in an nonaqueous solution to provide inexpensive and high-performance batteries.

[0017] The active material according to the present invention has a layer structure similar to the structure of LiNiO_2 or LiCoO_2 , i.e., a structure similar to $\alpha\text{-NaFeO}_2$.

[0018] The layered structure of the active material can be described from a packing MnO_2 slabs built up of edge-sharing MnO_6 octahedra in between which lithium ions are located in the octahedral oxygen environment. This structure comprises a layer of manganese ions in octahedral environment surrounded by oxygen ions arranged in a cubic close packed arrangement resulting in the formation of sheets of edge-shared octahedra. It also comprises a lithium layer where lithium is having an octahedral environment and is sandwiched between two layers of octahedral MnO_6 .

[0019] The active material according to the present invention was found to have a layer structure having a lattice constant of $a=2.86 \text{ \AA}$ and $c=14.23 \text{ \AA}$ similarly to LiNiO_2 or LiCoO_2 . The lattice constant is not a fixed one. That is, the unit lattice constant is subject to variation from 2.76 to 2.96 \AA as for a , and from 14.13 to 14.33 \AA as for c according to the conditions of preparation or by addition of dopant such as nickel, cobalt, zinc, etc. The active material exhibits continuous discharge characteristics between 4.5 V and 2 V vs. Li/Li^+ .

[0020] The active material of the invention is preferably produced by dissolving or suspending a starting manganese salt in lithium solution and causing the solution to react in an autoclave under high pressure and low pH solution. Suitable raw manganese materials are inorganic salts such as MnO_2 , Mn_2O_3 , MnOOH , and MnCO_3 , and organic salts such as manganese acetate, manganese butyrate, manganese oxalate, and manganese citrate. Suitable raw lithium materials are LiOH , LiNO_3 , Li_2CO_3 , Li_2O , lithium acetate, lithium butyrate, lithium oxalate, and lithium citrate. Solvents to be used in the reaction are purified water, and organic solvents such as ethyl alcohol, methyl alcohol, acetone, and acetonitrile. The reaction is preferably carried out at a high temperature of from 100 to 300°C.

[0021] LiMnO_2 having a layer structure can be synthesized by a hydrothermal process. The high-pressure and low-temperature hydrothermal process according to the present invention is also applicable to synthesis of other substances having a layer structure represented by general formula AMeO_2 (A: Li, Na or K; Me: Mn, Ni, Co, Fe, Cr or V).

EXAMPLES

[0022] The present invention will be described in greater detail with reference to examples, but it should be understood that the present invention is not constructed as being limited thereto.

[0023] 668 mg of LiOH was dissolved in 120 ml of water at 50°C, and thereafter, 50 mg of γ -MnO₂ was immersed therein for 30 minutes. The pH of the solution was adjusted to 1 to 2 and the mixture was heated in an

polytetrafluoroethylene-covered stainless steel autoclave at 170°C and 300 atm for 5 days to obtain lithium manganate according to the present invention.

[0024] The X-ray diffraction pattern (CuK α) of the resulting active material is shown in Fig. 1A. For comparison, the diffraction pattern of LiNiO₂ having a layer structure is shown in Fig. 1B, and that of orthorhombic LiMnO₂ obtained by a conventional solid phase reaction (calcination of a mixture of γ -MnO₂ and LiOH at 700°C) is shown in Fig. 1C.

[0025] It can be seen that the diffraction pattern of the active material of the present invention is not similar to that of known orthorhombic LiMnO₂ but to that of LiNiO₂ having a layer structure. It was found that the indices of a plane of the diffraction peaks can be assigned to the layer structure of hexagonal system having a space group of R3m. The structural description of the active material of the invention is shown in Fig. 2.

[0026] The active material of the present invention has a packing structure of two MnO₂ layers composed of octahedral of MnO₆ sharing edges, in which a lithium ion is surrounded by oxygen ions having an octahedral coordination. In this structure, manganese ions are arranged in layers and surrounded by an octahedron of oxygen ions which are arranged in cubic closest packing to form an octahedral layer sharing edges. The lithium ion of the lithium layer is sandwiched in between two layers of octahedral of MnO₆.

[0027] It was found that the structure of the active material of the present invention is similar to the layer structure of LiNiO₂ or LiCoO₂, typically having a unit lattice constant of $a=2.86 \text{ \AA}$ and $c=14.23 \text{ \AA}$. The unit volume was 101.23 \AA^3 , approximately the same as 101.3 \AA^3 of LiNiO₂. This means that the LiMnO₂ having a layer structure and LiNiO₂ are apt to form a solid solution. In fact, addition of nickel to LiMnO₂ results in stabilization of crystal properties, and the resulting solid solution was less susceptible to deterioration by charge and discharge cycles.

[0028] On the other hand, because of structural difference between orthorhombic LiMnO₂ and LiNiO₂, orthorhombic LiMnO₂ forms a solid solution LiMn_xNi_{1-x}O₂ ($0 \leq x \leq 0.5$), but the solid solution has poor charge and discharge characteristics as reported in Solid State Ionics, 57(1992)311. It was confirmed that addition of cobalt to the active material of the invention produces the same effect. It is understood that the LiMnO₂ having a layer structure according to the invention is different from

LiMnO₂ of orthorhombic structure the diffraction pattern of which is shown in Fig. 1C.

[0029] The active material obtained in this Example had a layer structure of perfect hexagonal system in which no substitution between manganese ions and lithium ions was observed. While structures in which lithium and manganese are substituted with each other were obtained in some cases depending on the temperature and pressure conditions of the hydrothermal reaction, the active material principally had a layer structure.

[0030] A battery was prepared using thus obtained active material as a positive electrode active material and metallic lithium as a negative electrode. When the battery was charged to 4.2 V at a current of 0.2 C and then discharged to 2 V at the same current, satisfactory electrochemical activity was exhibited. The typical discharge characteristics are shown in Fig. 3. It is seen that stable discharge characteristics can be secured through the charge and discharge cycles. It is also seen that continuous discharge characteristics are exhibited between 4.5 V and 2 V vs. Li/Li⁺, which has not been reported to date. The LiMnO₂ having a layer structure has now been proved to be an unreported inexpensive active material. The LiMnO₂ has a theoretical capacity density of 286 mAh/g. Further optimization of electrode designing will produce higher performance.

[0031] While the present invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the scope thereof.

Claims

1. A positive electrode active material for lithium batteries comprising lithium manganate having the formula LiMnO₂ and having a hexagonal structure and a space group of R3m, and exhibiting continuous discharge voltage characteristics between 4.5 V and 2 V vs. Li/Li⁺, with the proviso that said positive electrode active material does not contain a mixture of LiMnO₂ and LiMn₂O₄.
2. A positive electrode active material according to claim 1, wherein said lithium manganate has a unit lattice constant of $a=2.76$ to 2.96 \AA and $c=14.13$ to 14.33 \AA .
3. A positive electrode active material according to claim 1, further comprising at least one of nickel, cobalt, iron, chromium, zinc and vanadium.
4. A battery comprising a positive electrode active material for lithium batteries comprising lithium manganate having the formula LiMnO₂ and having a hexagonal structure and a space group of R3m, and exhibiting continuous discharge voltage character-

istics between 4.5 V and 2 V vs. Li/Li^+ , and a negative electrode, with the proviso that said positive electrode active material does not contain a mixture of LiMnO_2 and LiMn_2O_4 .

- 5 A battery according to claim 4, wherein said negative electrode comprises metallic lithium, carbon and metal alloys.
- 6 A battery according to claim 4, wherein said lithium manganate has a unit lattice constant of $a=2.76$ to 2.96 \AA and $c=14.13$ to 14.33 \AA .
- 7 A battery according to claim 4, wherein said positive electrode active material further comprises at least one of nickel, cobalt, zinc, iron, chromium and vanadium.
- 8 A method for producing a positive electrode active material for lithium batteries wherein a raw manganese material and a raw lithium material are reacted by a hydrothermal process to produce a lithium manganate, wherein said hydrothermal process is carried out at a temperature between 100°C and 300°C .
- 9 A method according to claim 8, wherein said raw manganese material is selected from a group consisting of MnO_2 , Mn_2O_3 , MnOOH , MnCO_3 , manganese acetate, manganese butyrate, manganese oxalate, and manganese citrate, and said raw lithium materials is selected from a group consisting of LiOH , LiNO_3 , Li_2CO_3 , Li_2O , lithium acetate, lithium butyrate, lithium oxalate, and lithium citrate.
- 10 A method according to claim 8, wherein said hydrothermal process is carried out in a solvent selected from purified water, ethyl alcohol, methyl alcohol, acetone, and acetonitrile.

Patentansprüche

1. Aktivmaterial für eine positive Elektrode für eine Lithiumbatterie, umfassend Lithiummanganat, dargestellt durch die Formel LiMnO_2 , wobei das Lithiummanganat durch eine hexagonale Struktur mit der Raumgruppe $R3m$ gekennzeichnet ist und wobei das Aktivmaterial durch eine kontinuierliche Entladecharakteristik bei einer Entladespannung im Bereich von 4,5 V bis 2 V gegen Li/Li^+ gekennzeichnet ist, mit der Maßgabe, dass das Aktivmaterial für die positive Elektrode kein Gemisch aus LiMnO_2 und LiMn_2O_4 umfasst.
2. Aktivmaterial für eine positive Elektrode nach Anspruch 1, wobei das Lithiummanganat durch die Gitterkonstanten $a = 2,76$ bis $2,96 \text{ \AA}$ und $c = 14,13$

bis $14,33 \text{ \AA}$ gekennzeichnet ist.

3. Aktivmaterial für eine positive Elektrode nach Anspruch 1, weiterhin umfassend mindestens einen Bestandteil, ausgewählt aus Nickel, Cobalt, Eisen, Chrom, Zink und Vanadium.
4. Lithiumbatterie mit einer positiven Elektrode und einer negativen Elektrode, wobei die positive Elektrode ein Aktivmaterial umfasst, umfassend Lithiummanganat, dargestellt durch die Formel LiMnO_2 , wobei das Lithiummanganat durch eine hexagonale Struktur mit der Raumgruppe $R3m$ gekennzeichnet ist und wobei das Aktivmaterial durch eine kontinuierliche Entladecharakteristik bei einer Entladespannung im Bereich von 4,5 V bis 2 V gegen Li/Li^+ gekennzeichnet ist, mit der Maßgabe, dass das Aktivmaterial der positiven Elektrode kein Gemisch aus LiMnO_2 und LiMn_2O_4 umfasst.
5. Batterie nach Anspruch 4, wobei die negative Elektrode metallisches Lithium, Kohlenstoff oder eine Metalllegierung umfasst.
6. Batterie nach Anspruch 4, wobei das Lithiummanganat durch die Gitterkonstanten $a = 2,76$ bis $2,96 \text{ \AA}$ und $c = 14,13$ bis $14,33 \text{ \AA}$ gekennzeichnet ist.
7. Batterie nach Anspruch 4, wobei das Aktivmaterial der positiven Elektrode weiterhin mindestens einen Bestandteil umfasst, ausgewählt aus Nickel, Cobalt, Zink, Eisen, Chrom und Vanadium.
8. Verfahren zur Herstellung eines Aktivmaterials für eine positive Elektrode für eine Lithiumbatterie, umfassend das Umsetzen eines Manganausgangsmaterials und eines Lithiumausgangsmaterials unter Anwendung eines Hydrothermalverfahrens, um Lithiummanganat herzustellen, wobei das Hydrothermalverfahren bei einer Temperatur im Bereich von 100°C bis 300°C durchgeführt wird.
9. Verfahren nach Anspruch 8, wobei das Manganausgangsmaterial aus MnO_2 , Mn_2O_3 , MnOOH , MnCO_3 , Manganacetat, Manganbutyrat, Manganoxalat und Mangancitrat ausgewählt wird, und wobei das Lithiumausgangsmaterial aus LiOH , LiNO_3 , Li_2CO_3 , Li_2O , Lithiumacetat, Lithiumbutyrat, Lithiumoxalat und Lithiumcitrat ausgewählt wird.
10. Verfahren nach Anspruch 8, wobei die Umsetzung in einem Lösungsmittel, ausgewählt aus gereinigtem Wasser, Ethylalkohol, Methylalkohol, Aceton und Acetonitril, durchgeführt wird.

Revendications

1. Matière active d'électrode positive pour des batteries au lithium comprenant du manganate de lithium ayant la formule LiMnO_2 et ayant une structure hexagonale et un groupe d'espace de $R3m$, et présentant des caractéristiques de tension de décharge continue entre 4,5 V et 2 V par rapport à Li/Li^+ , à condition que ladite matière active d'électrode positive ne contienne pas de mélange de LiMnO_2 et de LiMn_2O_4 . 5
2. Matière active d'électrode positive selon la revendication 1, dans laquelle ledit manganate de lithium a une constante de réseau de la maille cristalline de $a=2,76$ à $2,96$ Å et $c=14,13$ à $14,33$ Å. 15
3. Matière active d'électrode positive selon la revendication 1, comprenant en outre au moins un des éléments suivants : nickel, cobalt, fer, chrome, zinc et vanadium. 20
4. Batterie comprenant une matière active d'électrode positive pour des batteries au lithium comprenant du manganate de lithium ayant la formule LiMnO_2 et ayant une structure hexagonale et un groupe d'espace de $R3m$, et présentant des caractéristiques de tension de décharge continue entre 4,5 V et 2 V par rapport à Li/Li^+ , et une électrode négative, à condition que ladite matière active d'électrode positive ne contienne pas de mélange de LiMnO_2 et de LiMn_2O_4 . 25
5. Batterie selon la revendication 4, dans laquelle ladite électrode négative comprend du lithium métallique, du carbone et des alliages de métaux. 35
6. Batterie selon la revendication 4, dans laquelle ledit manganate de lithium a une constante de réseau de la maille cristalline de $a=2,76$ à $2,96$ Å et $c=14,13$ à $14,33$ Å. 40
7. Batterie selon la revendication 4, dans laquelle ladite matière active d'électrode positive comprend en outre au moins un des éléments suivants : nickel, cobalt, zinc, fer, chrome et vanadium. 45
8. Procédé de production d'une matière active d'électrode positive pour des batteries au lithium dans lequel on fait réagir une matière première du manganèse et une matière première du lithium dans un procédé hydrothermal pour produire un manganate de lithium, où on réalise ledit procédé hydrothermal à une température comprise entre 100°C et 300°C . 50
9. Procédé selon la revendication 8, où ladite matière première du manganèse est sélectionnée dans un groupe constitué de MnO_2 , Mn_2O_3 , MnOOH , 55

MnCO_3 , l'acétate de manganèse, le butyrate de manganèse, l'oxalate de manganèse et le citrate de manganèse, et ladite matière première du lithium est sélectionnée dans un groupe constitué de LiOH , LiNO_3 , Li_2CO_3 , Li_2O , l'acétate de lithium, le butyrate de lithium, l'oxalate de lithium, et le citrate de lithium.

10. Procédé selon la revendication 8, où on réalise ledit procédé hydrothermal dans un solvant sélectionné parmi l'eau purifiée, l'alcool éthylique, l'alcool méthylique, l'acétone et l'acétonitrile.

FIG. 1C

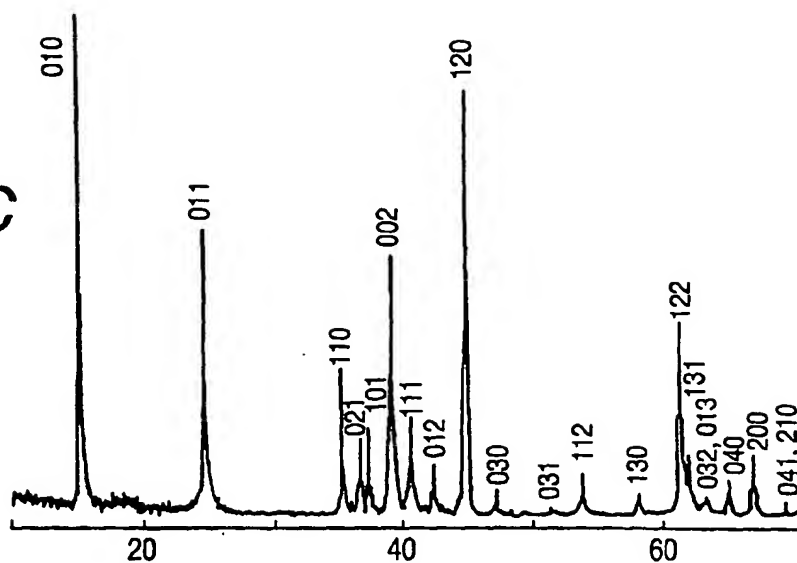


FIG. 1B

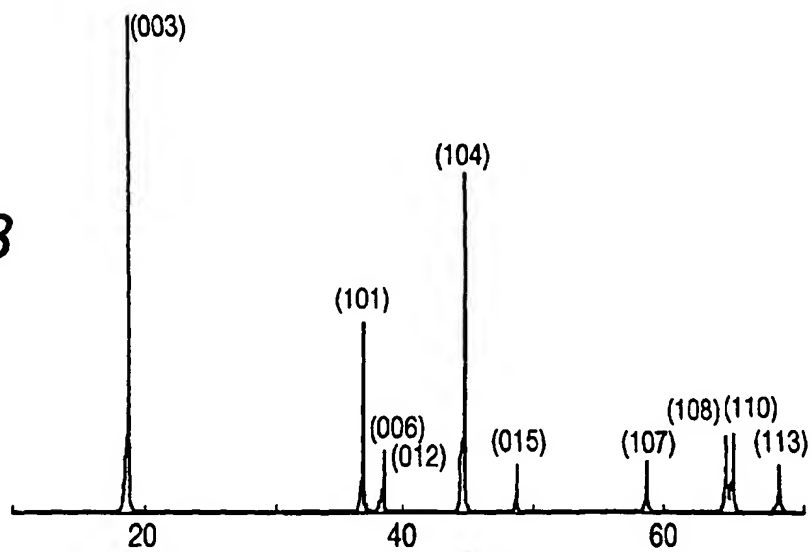


FIG. 1A

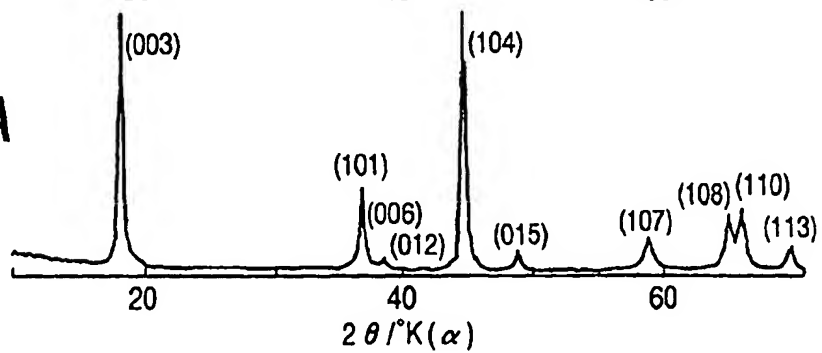


FIG. 2

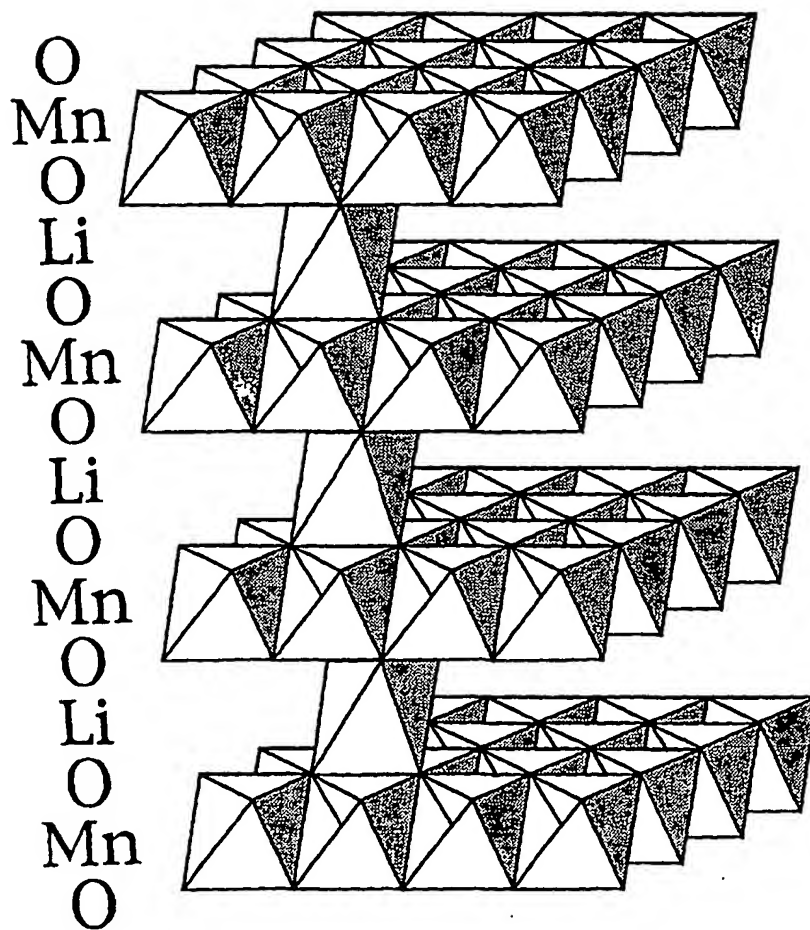


FIG. 3

